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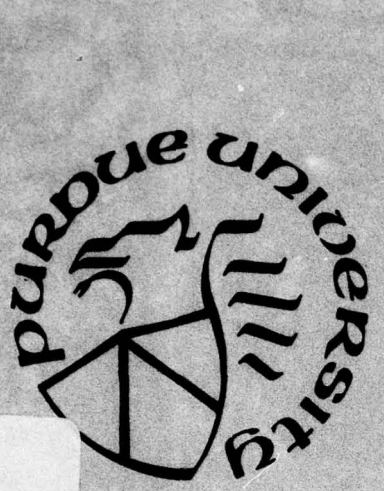

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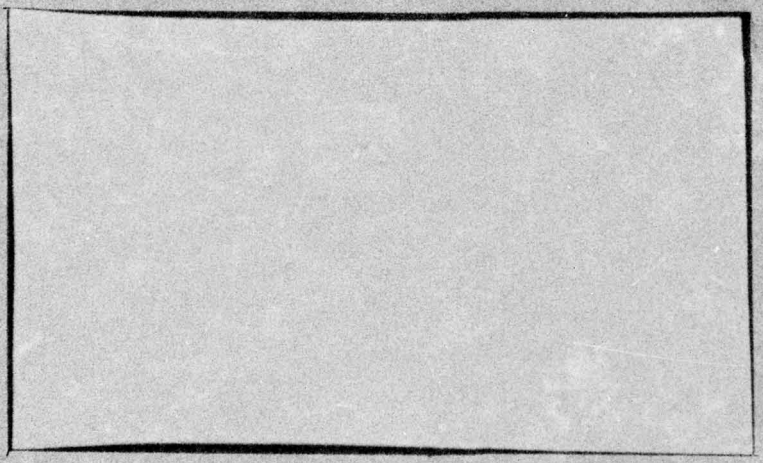

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THE EFFECTS OF SUBSTRATE COMPOSITION
ON THICK FILM CIRCUIT RELIABILITY.

10 R. W. Vest

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For the period 8/1/76 - 10/31/76

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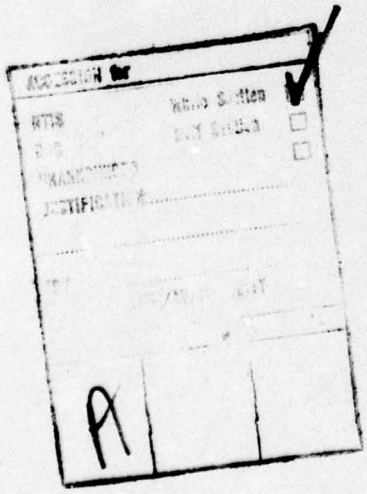

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FORWARD

Research described in this report constitutes the third three months of effort under a contract with the Naval Air Systems Command, Department of the Navy, under the technical cognizance of James Willis. The research was conducted in the Turner Laboratory for Electroceramics, School of Materials Engineering and School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907, under the direction of Professor R. W. Vest. Contributing to the Project were Assistant Professor G. L. Fuller, and Messrs. J. L. Himelick, W. S. Machin, and R. L. Reed.

ABSTRACT

During this quarter studies of the rate of the dissolution of 99.5% Al_2O_3 substrates (AlSiMag 772) in the model glass (63% PbO, 25% B_2O_3, 12% SiO_2) were conducted as a function of time at 800°C. The results were similar to those reported earlier for 96% Al_2O_3 substrates (AlSiMag 614) and were consistent with the proposed rate limiting steps of phase boundary reaction rate control at short times and diffusion through a boundary layer under natural convection at longer times. The dissolution rate of AlSiMag 614 substrates was measured at short contact times (3-15 minutes) by atomic absorption techniques and were in good agreement with values predicted by extrapolation of longer time data at 800°C. Studies of the distribution of substrate ingredients throughout the resistor glass at 800°C as a function of time showed that the boundary zone at the interface across which the concentrations change has a width of approximately 3 μm and is independent of contact time. Studies of the influence of substrate constituents dissolved in the glass on electrical properties of resistors uncovered a significant effect on temperature coefficient of resistance (TCR). A low TCR characteristic of reliable thick film resistors cannot be achieved with the model system unless an appreciable amount of substrate material is dissolved in the resistor glass.

TABLE OF CONTENTS

Section		Page
1	Introduction	1
2	Substrate-Glass Reaction Kinetics	2
	2.1 Rate of Substrate Dissolution	2
	2.1.1 AlSiMag 772 Substrates	2
	2.1.2 Short Contact Times	4
	2.2 Rate of Substrate Diffusion	9
3	Electrical Properties	11
4	Future Plans	17
5	References	17
6	Statement of Estimated Costs	18

1. INTRODUCTION

The print and fire processing of thick film circuits ensures that there will always be some degree of chemical interaction between the film and the substrate because all common substrate materials are soluble to some degree in the glass used in thick film inks. This interaction is primarily responsible for the development of adhesion between the thick film resistor and the substrate. By virtue of the resistor-substrate interaction, the composition of the glass is changed, and as a consequence all of the physical properties of the glass will change to some extent. These changes in physical properties of the glass will result in modified kinetics for the various microstructure development processes in thick film resistors, and all electrical properties of the resistors are related to their microstructure. This research program is directed toward the determination of the effects of the major constituent, common additives, and impurities in alumina substrates on the kinetics of microstructure development, electrical characteristics and the adhesion of thick film resistors.

Research on this project is divided into two general areas: 1) resistor-substrate interaction kinetics; and 2) the influence of the substrate on microstructure development and electrical properties. The goal of the first area is to determine what fraction of a fired resistor is made up of material which came from the substrate, and how the substrate material is distributed throughout the resistor. The goal of the second area is to determine the influence of constituents derived from the substrate on various electrical properties, with primary emphasis on those properties most intimately related to reliability in use. The model resistor system being utilized is RuO_2 conductive with 63% PbO, 25% B_2O_3, 12% Al_2O_3 glass. This

system has been very thoroughly studied and the materials properties and electrical behavior thoroughly characterized. The second system to be studied will be a quasi-commercial system employing $Bi_2Ru_2O_7$ conductive and an appropriate glass.

2. SUBSTRATE-GLASS REACTION KINETICS

2.1 Rate of Substrate Dissolution

2.1.1 AlSiMag 772 Substrates

The experimental procedure for determining the rate of substrate dissolution in the glass by following the weight change of the substrate was described in Quarterly Technical Report No. 1 [1] and the data analysis technique was described in Quarterly Technical Report No. 2 [2]. The experimental results for AlSiMag 614 (96% Al_2O_3) substrates could be represented by two straight line segments on a substrate recession (Y) versus time plot over the temperature range 750 to 1000°C for contact times in excess of 15 minutes. Identical measurements were carried out with AlSiMag 772 (99.5% Al_2O_3) substrates in contact with the standard glass (63% PbO, 25% B_2O_3, 12% SiO_2) at 800°C, and the results are shown in Fig. 1. Where more than one experiment was conducted at a given contact time, vertical bars represent the maximum and minimum value of Y, and the solid dot represents the mean value of the measurements.

The three possible mechanisms for the rate controlling step in the dissolution process require either a linear or a $t^{1/2}$ dependence for Y [2]. The $t^{1/2}$ dependence could not be fit to the data shown in Fig. 1 over any portion of time, and the best analytical representation was found to be a linear dependence at short times changing to another linear dependence with a smaller slope at longer times.

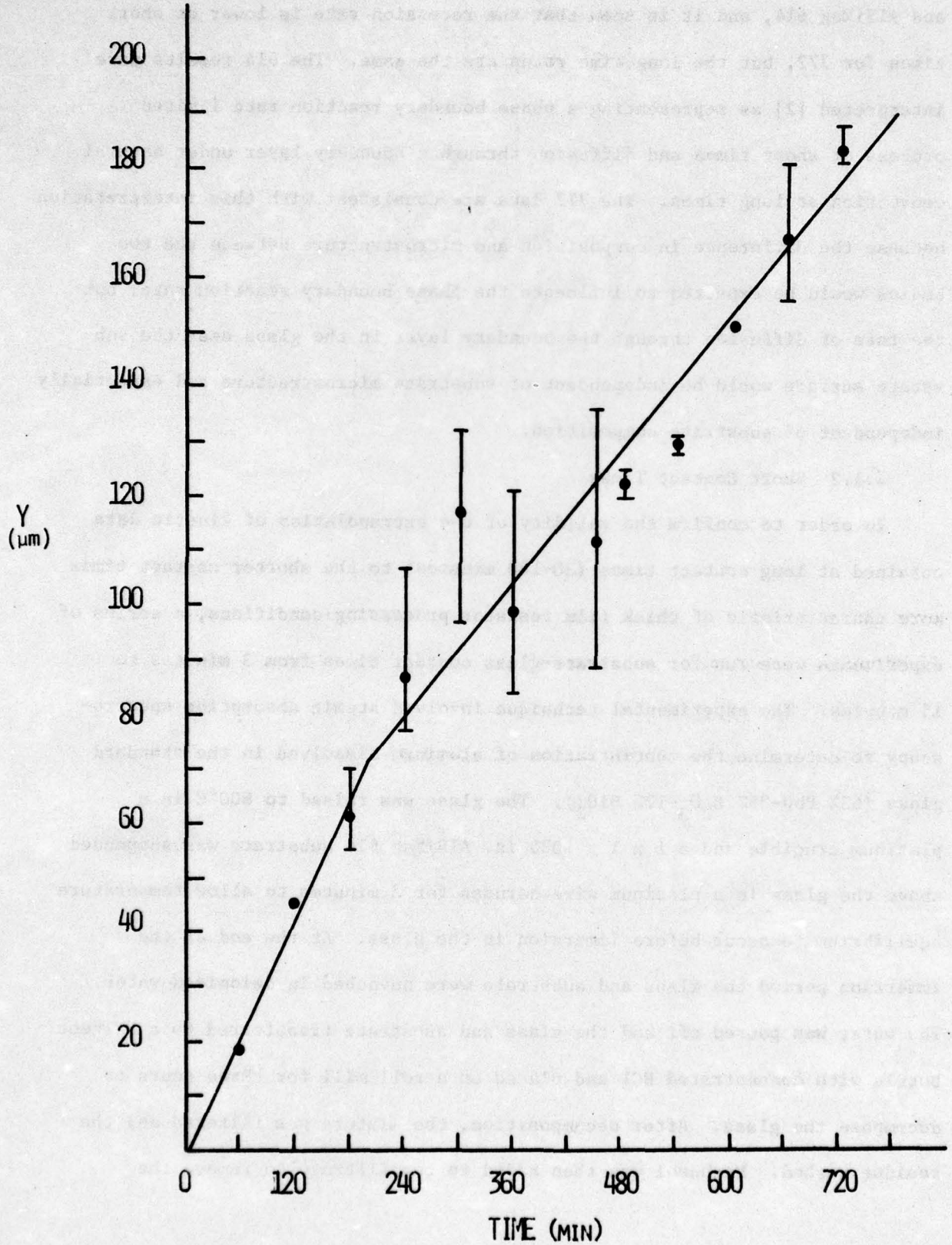

FIGURE 1. DISSOLUTION OF ALSIMAG 772 AT 800°C

Figure 2 is a comparison of the linear recession rate for AlSiMag 772 and AlSiMag 614, and it is seen that the recession rate is lower at short times for 772, but the long time rates are the same. The 614 results were interpreted [2] as representing a phase boundary reaction rate limited process at short times and diffusion through a boundary layer under natural convection at long times. The 772 data are consistent with this interpretation because the difference in composition and microstructure between the two bodies would be expected to influence the phase boundary reaction rate, but the rate of diffusion through the boundary layer in the glass near the substrate surface would be independent of substrate microstructure and essentially independent of substrate composition.

2.1.2 Short Contact Times

In order to confirm the validity of the extrapolation of kinetic data obtained at long contact times (30-180 minutes) to the shorter contact times more characteristic of thick film resistor processing conditions, a series of experiments were run for substrate-glass contact times from 3 minutes to 15 minutes. The experimental technique involved atomic absorption spectroscopy to determine the concentration of aluminum dissolved in the standard glass (63% PbO-25% B_2O_3-12% SiO_2). The glass was raised to 800°C in a platinum crucible and a 1 x 1 x .025 in. AlSiMag 614 substrate was suspended above the glass in a platinum wire harness for 3 minutes to allow temperature equilibrium to occur before immersion in the glass. At the end of the immersion period the glass and substrate were quenched in deionized water. The water was poured off and the glass and substrate transferred to a Nalgene bottle with concentrated HCl and placed on a roll mill for three hours to decompose the glass. After decomposition, the mixture was filtered and the residue washed. Methanol was then added to the filtrate to remove the

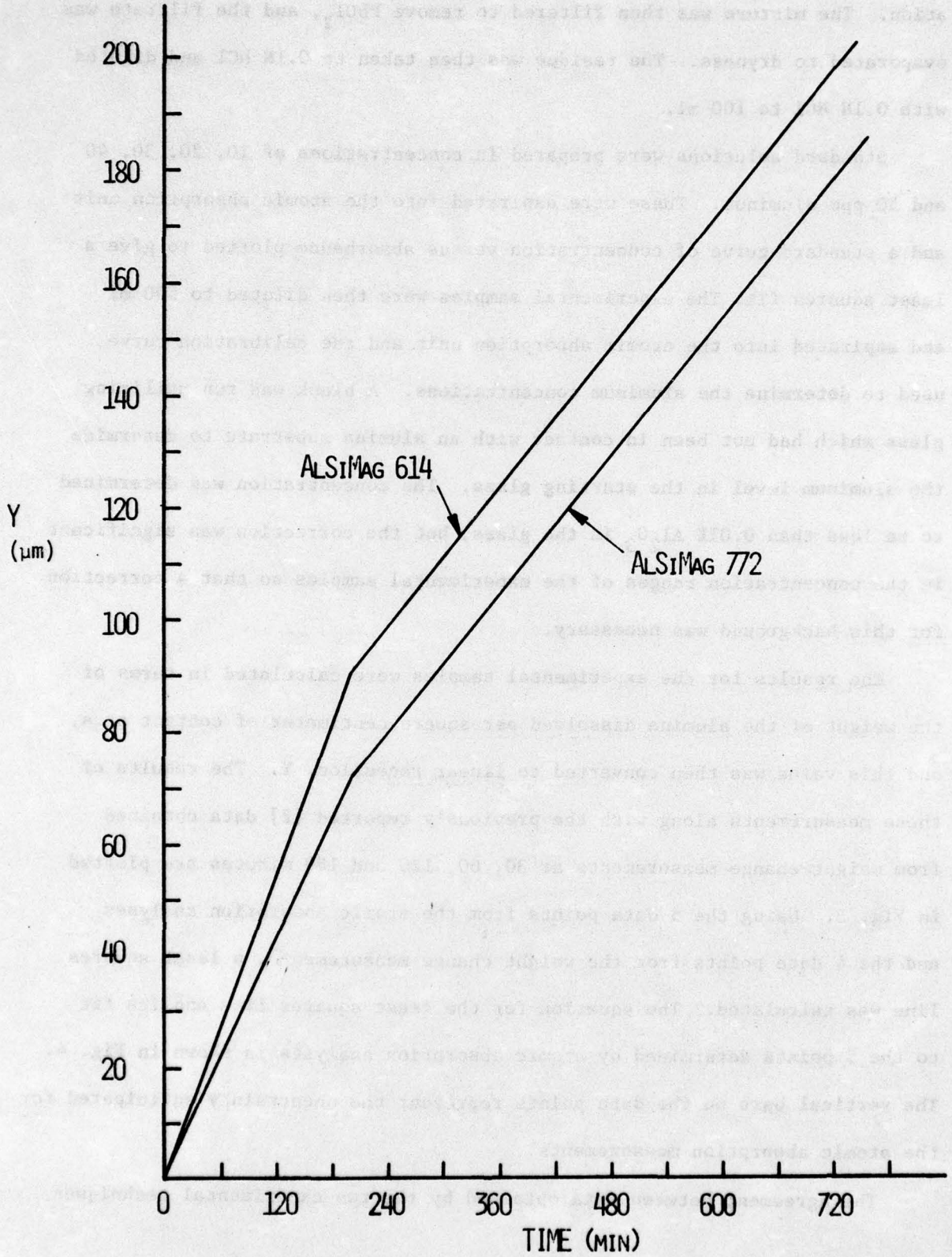

FIGURE 2. DISSOLUTION OF ALUMINA SUBSTRATES AT 800°C

borates and the filtrate was concentrated to approximately 20 ml by evaporation. The mixture was then filtered to remove $PbCl_2$, and the filtrate was evaporated to dryness. The residue was then taken to 0.1N HCl and diluted with 0.1N HCl to 100 ml.

Standard solutions were prepared in concentrations of 10, 20, 30, 40 and 50 ppm aluminum. These were aspirated into the atomic absorption unit and a standard curve of concentration versus absorbence plotted to give a least squares fit. The experimental samples were then diluted to 500 ml and aspirated into the atomic absorption unit and the calibration curve used to determine the aluminum concentrations. A blank was run utilizing glass which had not been in contact with an alumina substrate to determine the aluminum level in the starting glass. The concentration was determined to be less than 0.01% Al_2O_3 in the glass, but the correction was significant in the concentration ranges of the experimental samples so that a correction for this background was necessary.

The results for the experimental samples were calculated in terms of tne weight of the alumina dissolved per square centimeter of contact area, and this value was then converted to linear recession, Y. The results of these measurements along with the previously reported [2] data obtained from weight change measurements at 30, 60, 120 and 180 minutes are plotted in Fig. 3. Using the 5 data points from the atomic absorption analyses and the 4 data points from the weight change measurements, a least squares line was calculated. The equation for the least squares line and its fit to the 5 points determined by atomic absorption analyses is shown in Fig. 4. The vertical bars on the data points represent the uncertainty anticipated for the atomic absorption measurements.

The agreement between data obtained by the two experimental techniques

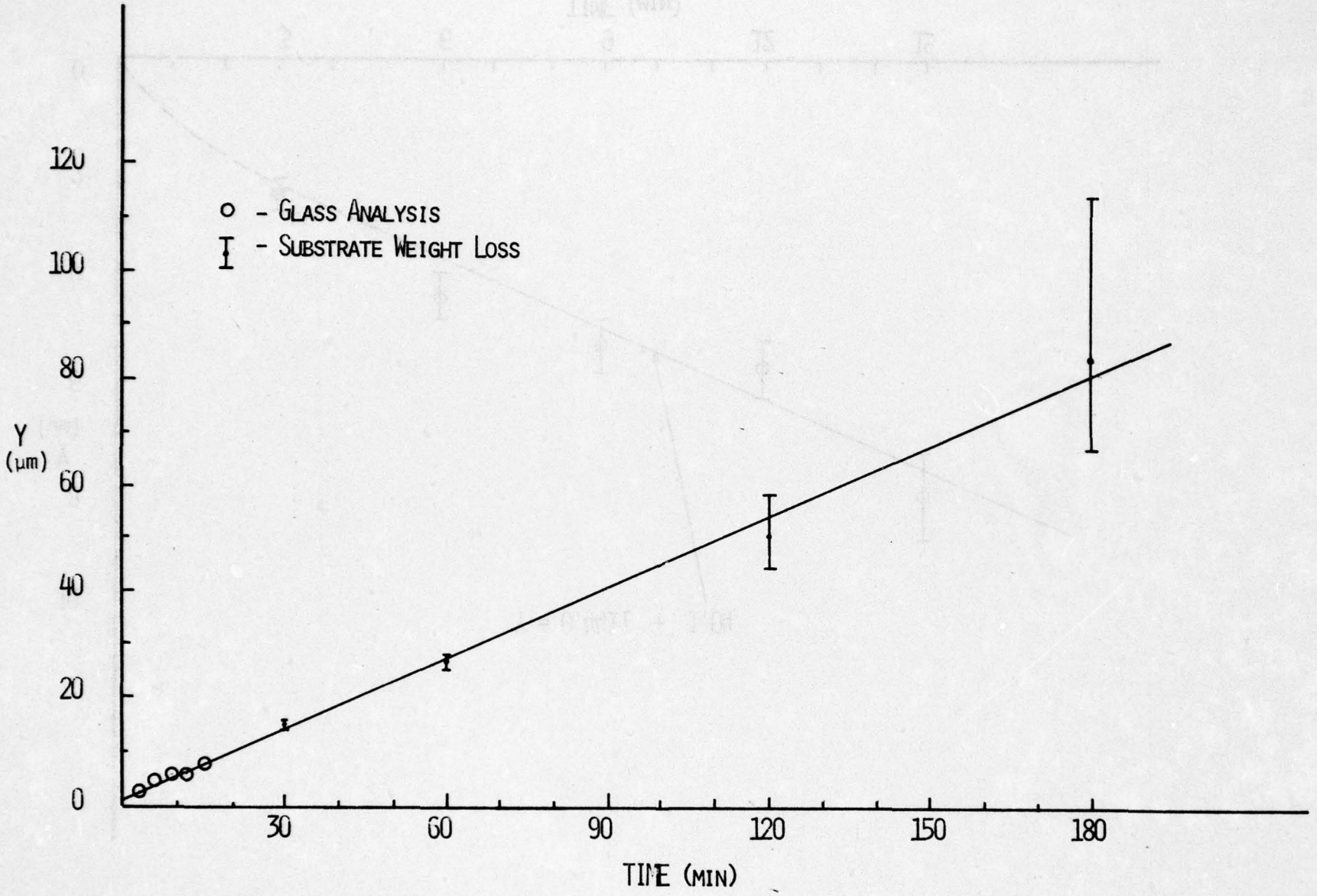

FIGURE 3. DISSOLUTION OF ALSIMAG 614 AT 800°C

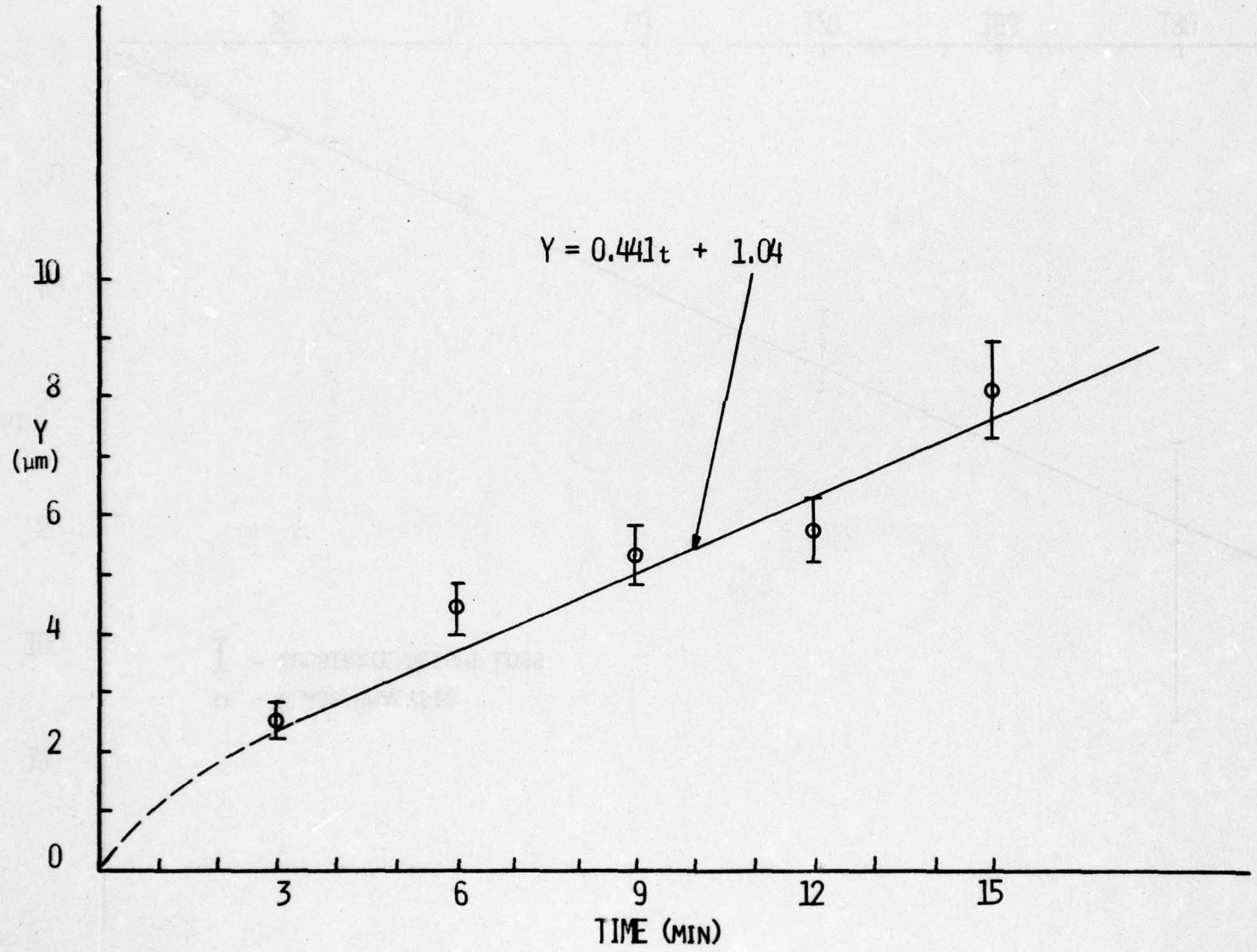

FIGURE 4. DISSOLUTION OF ALSIMAG 614 AT 800°C

is considered to be extremely good, but the least squares line does not pass through the origin. The time below 3 minutes is shown by a dashed curve in Fig. 4, and this behavior could be due to a different rate controlling step at very short times, but it also may be due to a small but systematic error in the atomic absorption analyses. A systematic error translated to 1 μm recession for each sample would bring the least squares line through the origin. Such an error is insignificant for the present project and will not be pursued further.

2.2 Rate of Substrate Diffusion

In order to correlate the amount of substrate materials dissolved in the glass and the electrical behavior of thick film resistors, it is also necessary to know the distribution of the substrate constituents in the glass as a function of processing conditions. The substrates for these diffusion studies were prepared by screen printing a formulation containing glass as the only inorganic ingredient and firing for appropriate times at 800°C. The formulation was such that a glass film approximately 13 μm thick was produced after firing. The substrates were scored on the back side with a diamond stylus and fractured before mounting for observation in the Scanning Electron Microscope (SEM). Figure 5 shows one of these samples and the apparent interface between the glass and the substrate is indicated. The unevenness of this interface is approximately the same as the surface roughness of the virgin substrates.

Selected areas of the substrate-glass interface region were magnified 5,000 to 10,000X in the SEM and points along various lines at varying distances from the interface were analyzed with the EDAX. All major components in both glass and substrate, with the exception of boron and oxygen, were silultaneously analyzed by calling up the appropriate computer program.

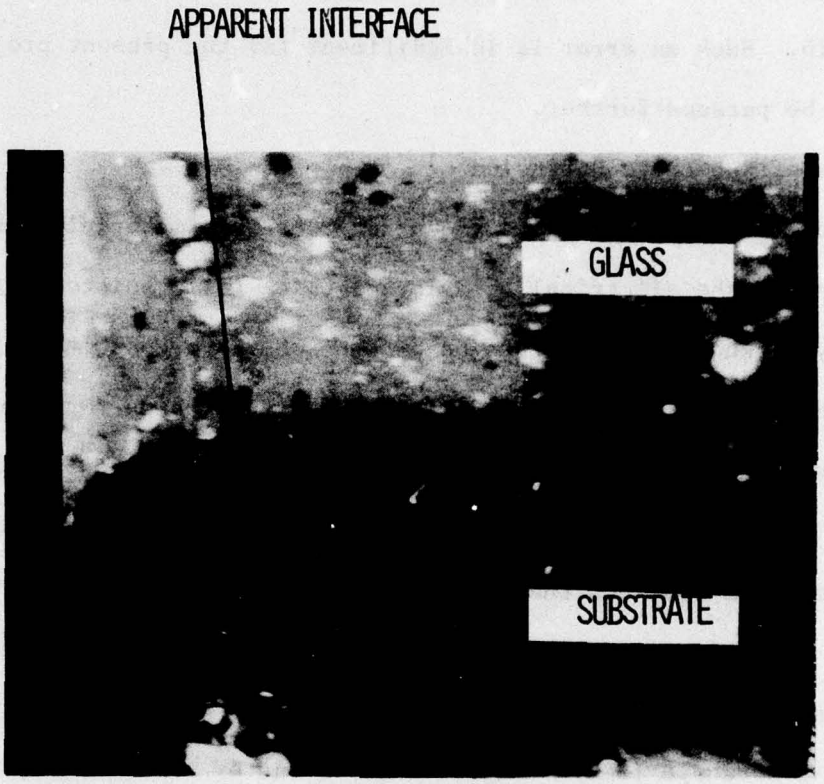

FIGURE 5. FRACTURE SURFACE SHOWING SUBSTRATE-GLASS INTERFACE (6500X)

Results for samples fired for 4, 8, and 10 minutes at 800°C are shown in Figs. 6 through 8 respectively. Only the Al_2O_3 and PbO profiles are plotted, but the other glass and substrate constituents showed similar profiles. The concentration profiles at all three contact times suggest that the boundary zone at the interface across which the concentrations change has a width of approximately 3 μm and is independent of contact time. This conclusion is consistent with the mechanisms proposed for the dissolution kinetics, namely, that the rate of dissolution in this time regime is determined by a phase boundary reaction and that diffusion of dissolved species away from the boundary is fast by comparison.

The concentration of Al_2O_3 in the glass outside of the boundary zone is seen to be constant at all three contact times with the concentrations increasing with increasing contact time. The EDAX was not calibrated with standard samples so the absolute values of the concentrations are somewhat in question, but the Al_2O_3 concentrations in the bulk glass indicated in Figs. 6 - 8 are consistent with the values predicted from Fig. 4. Concentration profiles such as those shown in Figs. 6 - 8 will be utilized to calculate interdiffusion coefficients for both species.

3. ELECTRICAL PROPERTIES

The procedures for preparing glass frits containing varying amounts of substrate constituents were described in the preceeding report [2]. Mixtures of RuO_2 and glass powders were compacted by isostatic pressing to give composites approximately 0.1 x 0.4 x 1.3 cm. The composites were then placed in platinum foil boats and fired in two ways: Type 1 samples were fired in a furnace at 800°C for 15 minutes, transferred to a second furnace at 450°C for a 1 hour anneal, and removed from the furnace to cool

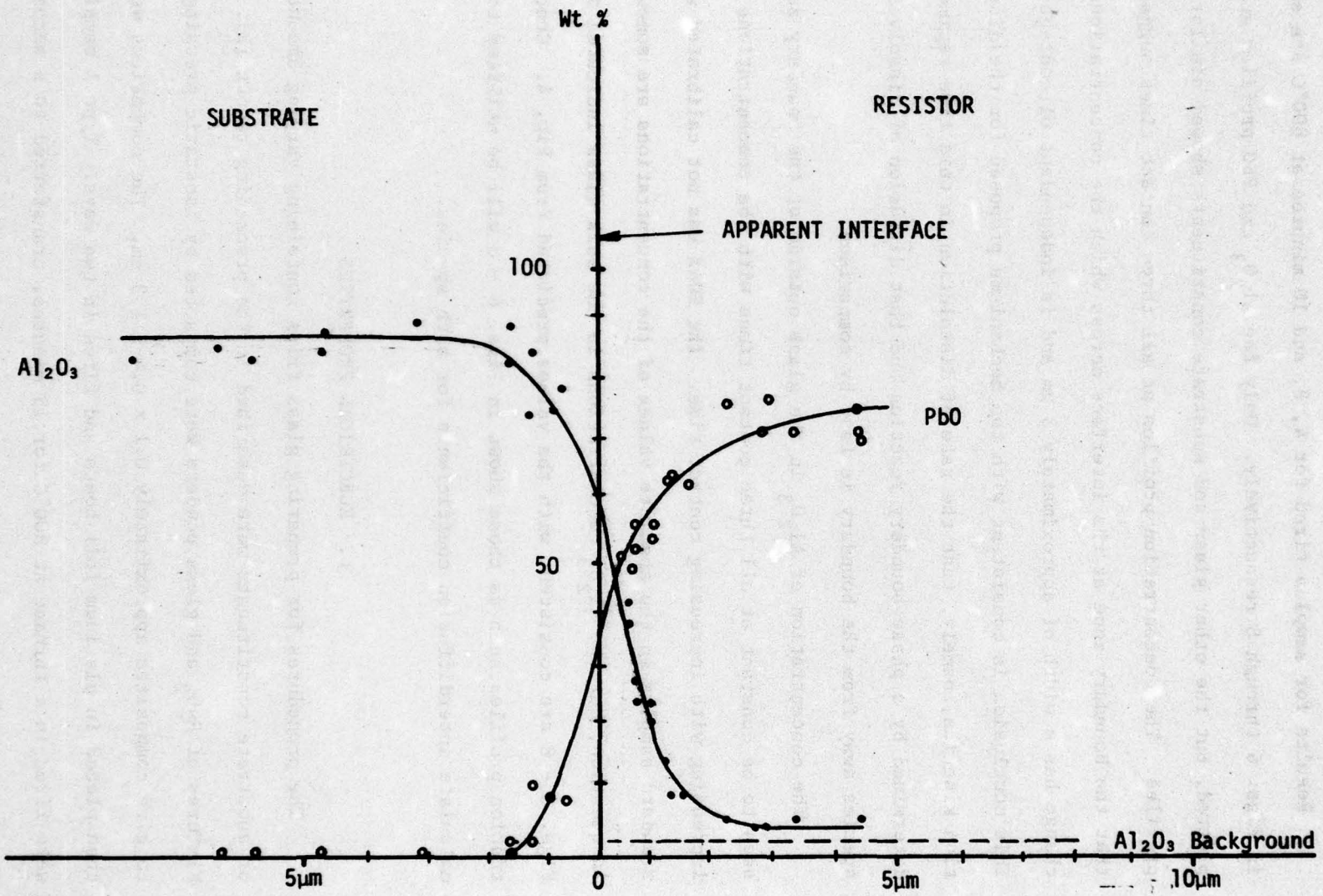

FIGURE 6. INTERDIFFUSION ACROSS RESISTOR-SUBSTRATE INTERFACE (800°C, 4 MINUTES)

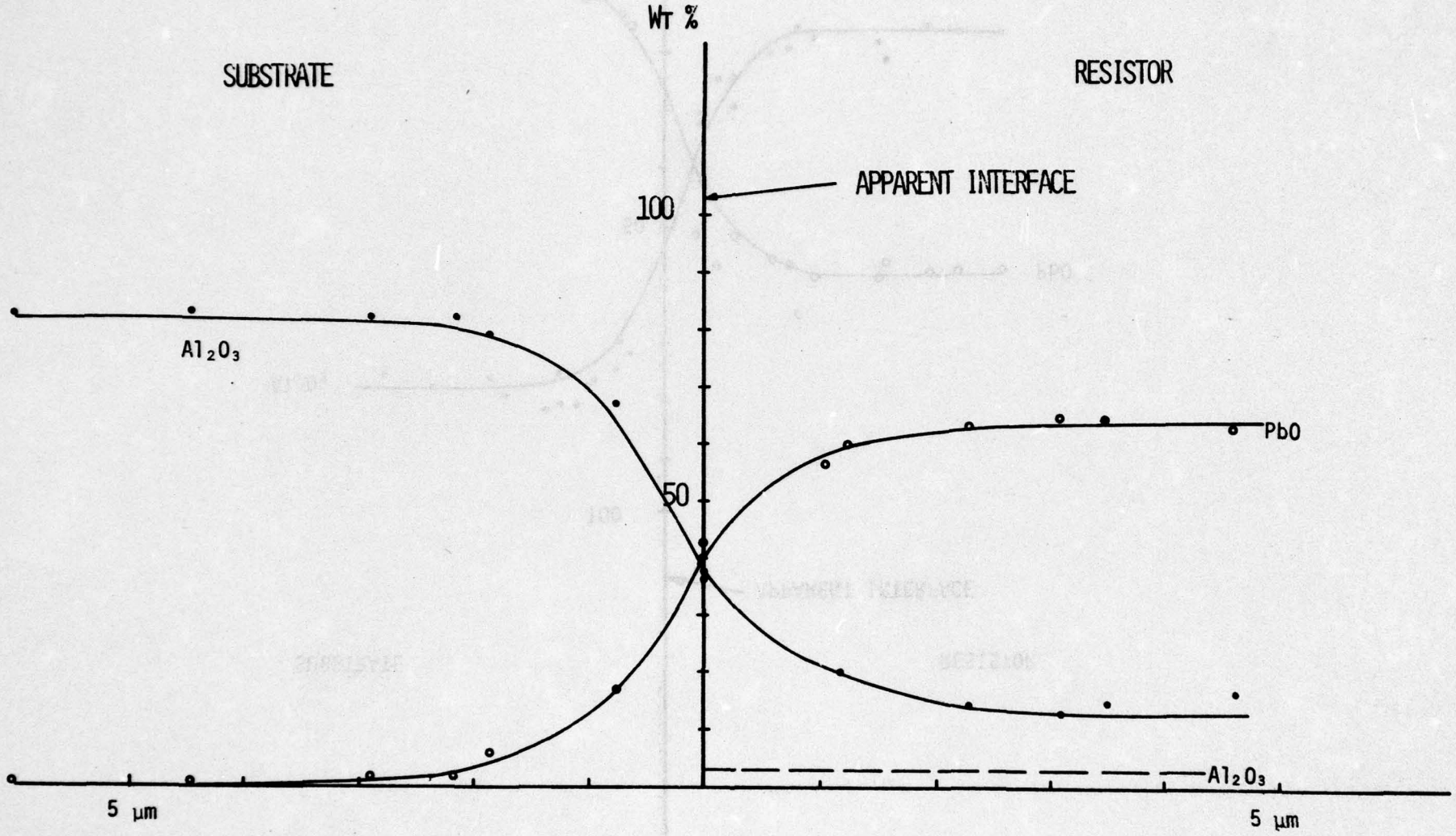

FIGURE 7. INTERDIFFUSION ACROSS RESISTOR-SUBSTRATE INTERFACE (800°C, 8 MINUTES)

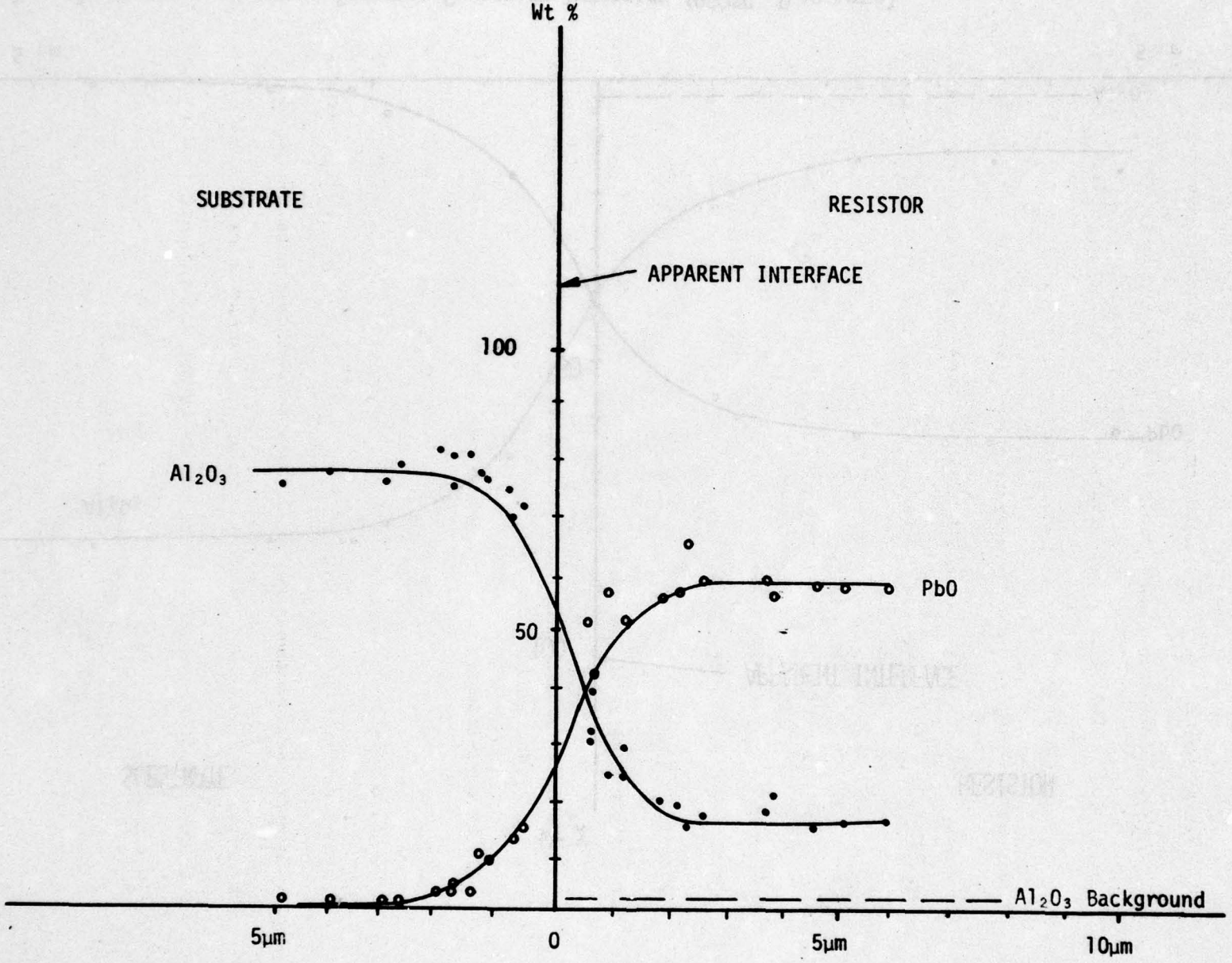

FIGURE 8. INTERDIFFUSION ACROSS RESISTOR-SUBSTRATE INTERFACE (800°C, 10 MINUTES)

at room temperature; Type 2 samples were fired in a push-rod furnace at a linear heating rate of 12.2°C per minute from room temperature to 800°C, held for 15 minutes, cooled at 50°C per minute to 450°C, held for 1 hour, and cooled at 26°C per minute to room temperature. After firing, the composites of both sample types were provided with silver electrodes and four terminal resistivity measurements were made from -55 to + 125°C. The results of these measurements (Fig. 9) were reduced to give normalized resistance as a function of temperature so that the TCR's* of the samples could be readily compared. Both sample types made from glass having no substrate dissolved in it showed good agreement with each other over the entire temperature range, and gave a hot TCR of +400 ppm/°C and a cold TCR of +360 ppm/°C. Considerably different behavior was observed for both sample types when the glass contained 8% substrate dissolved in it prior to fritting and grinding; sample Type 1 had a hot TCR of +28 ppm/°C and a cold TCR of -10 ppm/°C, while sample Type 2 had a hot TCR of +110 ppm/°C cold TCR of +25 ppm/°C.

The normalized resistance versus temperature curves shown in Fig. 9 for the samples containing substrate dissolved in the glass are typical of good thick film resistors, whereas the TCR for samples containing no substrate dissolved in the glass are much too large for most applications. It is apparent that the presence of substrate constituents dissolved in the glass is a necessary condition in order to achieve low TCR resistors with the model resistor system. Since TCR is one of the more critical parameters

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* The temperature coefficient of resistance (TCR) is defined as:

$$TCR = \frac{10^6}{R_{25°}} \frac{R_T - R_{25°}}{T - 25°} \quad \text{ppm/°C}$$

The hot TCR is computed for T = 125°C and the cold TCR computed for T = -55°C.

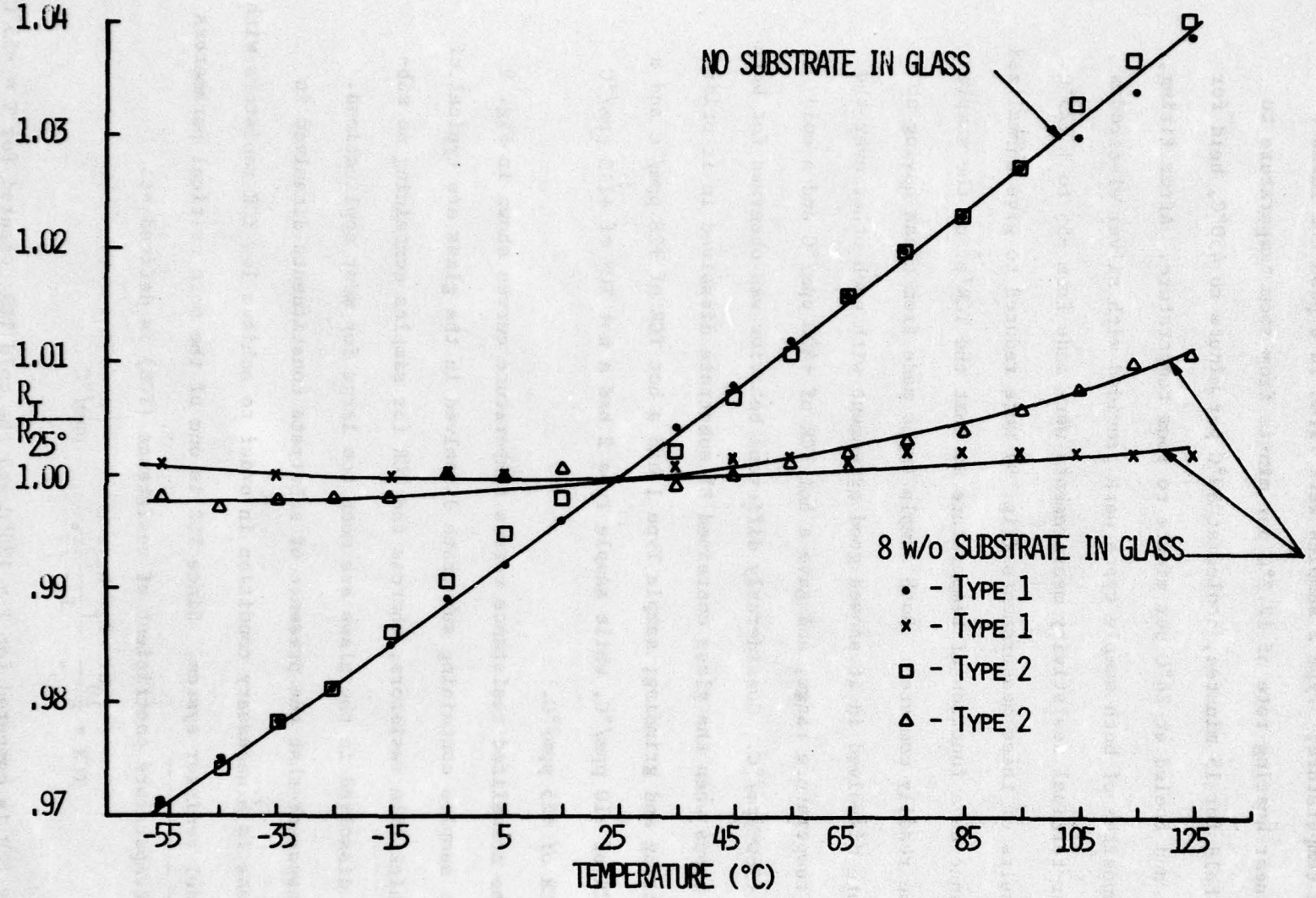

FIGURE 9. NORMALIZED RESISTANCE VERSUS TEMPERATURE FOR RuO_2-GLASS COMPOSITES

for satisfactory performance of thick film resistors in hybrid microcircuits, it follows that the compositional change of the glass arising from interactions with the substrate must be carefully controlled if a suitable degree of repeatability is to be achieved.

4. FUTURE PLANS

The studies of substrate dissolution kinetics will be extended to single crystal Al_2O_3 of at least two crystallographic orientations. The studies of electrical properties as a function of type and concentration of substrate constituents will be continued. The grain size distribution for the single lot AlSiMag 614 and AlSiMag 772 substrates will be determined.

5. REFERENCES

1. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Quarterly Report No. 1, NASC Contract No. N000 19-76-C-0354, 31 May 1976.

2. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Quarterly Report No. 2, NASC Contract No. N000 19-76-C-0354, 31 August 1976.

6. STATEMENT OF ESTIMATED COSTS

Contract No. N000 19-76-C-0354

February 1, 1976 - January 31, 1977

Beginning Fund Balance	$50,000.00
Funds Expended Through 10/31/76	35,548.47
Funds Remaining	$14,451.53

Planned Expenditures (Approximate)

November	$4800
December	$4800
January	$4800